Compression of Seven ScS Compositions with Sc Lattice Vacancies	X17C

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The early transition metal chalcogenides display a wide range of compositions formed via metal or chalcogen deficiency from a parent stoichiometry. The Sc_xS compositions ($0.8<x<1.0$) are such a system formed by vacancies in the metal sublattice of the rocksalt structure of Sc_1S.

Samples (synthesized by Tuenge [1]) from each composition were compressed to 50 GPa, at room temperature in a Mao-Bell [2] diamond anvil cell. Energy dispersive x-ray diffraction was done on beamline X17C with the detector at a 2θ angle of 15°. Pressures were determined by including a few specks of gold with the sample and using a standard equation of state for gold [3]. The pressure(P)-volume(V) data obtained were fit with fourth order Birch-Murnghan equations of state [4], to calculate thermodynamic parameters. Some of the equations of state thus obtained are shown in Fig. 1, and the thermodynamic parameters are shown in Fig. 2.

We usually expect phases with lattice vacancies to be more compressible than space-filled lattices, which are more dense. However, our experiments reveal the isothermal bulk moduli (Ko) increasing with increasing vacancy content. These observations were explained by the Extended Huckel calculations performed. The compositions with higher vacancy content have stronger, stiffer Sc-S bonds, because the higher oxidation state of Sc (>2) in the compositions with more vacancies, allow higher interaction of Sc 3d orbitals with S 3p orbitals [5,6].

The data obtained, and the P-V/Vo equations of state for each composition, start converging by about 40 GPa. In addition the unit cell volumes obtained after decompression from 50 GPa to below 20 GPa are higher than the pre- compression volumes for the compositions with more vacancies. We suggest that these effects are due to the formation of dumbells-shaped S pairs at very high pressure in the compositions with more Sc vacancies. If these pairs were retained upon decompression the Sc in the lattice would be reduced to an oxidation state closer to +2, giving less compact Sc-S bonds and resulting larger unit cell volumes.

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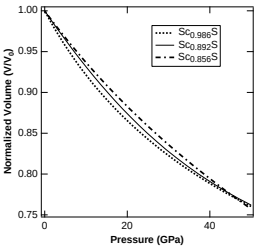

Figure 1. Pressure-Volume equations of state for three ScS compositions.

x in Sc_xS	Bulk Modulus K_0 (GPa)	$(\partial K_0/\partial P)$ K_0'	$(\partial K_0'/\partial P)$ K_0''
1.013±0.005	108±25	4±5	-5±1
0.986±0.005	104±14	4±3	3.7±0.5
0.892±0.003	135±18	0.8±0.4	17±3
0.875±0.006	130±29	1±5	24±5
0.864±0.006	148±22	-0.4±3	23±3
0.856±0.007	145±28	2±4	3.5±0.7
0.838±0.004	149±23	-2+3	44±7

Figure 2. Thermodynamic parameters obtained from P-V data.